Action: Air Monitoring of Volatile Organic Compounds (VOCs) near rendering facilities

Background and Objectives

Rendering facilities take animal parts and carcasses from livestock slaughter, poultry and meat packing operations, butcher shops and grocery stores and convert them into a host of beneficial products from soap to fertilizer to cosmetics and pet food. Several steps that are part of the rendering process can emit odors. Odor nuisances from the rendering facilities located in the Vernon area can impact the quality of life of individuals living in the East Los Angeles, Boyles Heights, West Commerce (ELABHWC) community. Animal parts and carcasses that are handled and processed outdoors and wastewater treatment systems cause a distinct unpleasant odor that can drift for miles and may result in headaches, nausea and respiratory irritation, impacting the quality of life of surrounding communities. South Coast AQMD's Rule 415 – Odors from Rendering Facilities – was specifically adopted to address this problem and reduce odors from rendering plants. This rule requires these facilities to conduct housekeeping practices and to install either permanent total enclosures or a closed system for certain processes to keep odors from drifting out of their buildings and into the community by 2022 or sooner.

There are five rendering facilities located in the Vernon area, namely: D&D Disposal/West Coast Rendering, Baker Commodities, Coast Packing Company, Clougherty Packing/Farmer Johns, and Darling Delaware (Figure 1). South Coast AQMD continues to conduct facility inspections to evaluate compliance with Rule 415 and respond to odor complaints. Responses to odor complaints include attempts to trace back the odors to a specific site or source and conduct follow up enforcement actions, where appropriate. It is often difficult to identify which facility is the source of an odor complaint in the community because these rendering plants are close to one another and because of the variable wind conditions in the area. Most sources of odors are difficult to measure, even with modern air monitoring techniques and, at times, the human nose can detect odors better than the most sophisticated air measurement equipment.

In order to address this air quality priority, the community requested mobile monitoring of volatile organic compounds (VOCs) and other odorous species near each rendering facility.

Method

To address this priority the South Coast AQMD evaluated the performance of a new specialized monitor that is capable of detecting VOCs and certain odorous compounds at very low concentrations. This instrument was installed in a mobile laboratory and used to conduct a series of near-source and community mobile monitoring covering all five identified rendering plants. As part of the AB 617 program, the South Coast AQMD contracted Aerodyne Research LLC to investigate this issue using its Aerodyne Mobile Laboratory, which is equipped with a suite of near-real-time, next-generation analytical equipment, capable of detecting trace-level VOCs, odorous compounds and a variety of other important air pollutants. These mobile measurements were performed to assess the extent to which emissions from these rendering facilities impact air quality in nearby communities (see Attachment A for details). South Coast AQMD is currently in the process of developing its own mobile platform, housing this next-generation instrument that is capable of simultaneous real-time monitoring of VOCs with high sensitivity to very low concentrations.

Also, a series of airborne surveys to search for gaseous pollutants hotspots, such as VOCs, methane, and ammonia were performed as part of the AB 617 program. To this end Aerospace Corporation conducted dedicated flights over central and east Los Angeles including the ELABHWC community (see Attachment A for details).

Results

- A series of airborne surveys were conducted by Aerospace Corporation over central and east Los Angeles (including the ELABHWC community) to identify hotspots of VOCs, methane, ammonia and other gaseous pollutants (Attachment A)
- On July 12, 2019, during one of these aerial surveys ammonia, methane, and sulfur dioxide hotspots were observed near the rendering facilities in ELABHWC (Attachment B)
- South Coast AQMD worked with Aerodyne Research LLC to conduct mobile measurements of VOCs near each of the five rendering facilities in ELABHWC. Mobile measurements were taken using state-of-the-art Proton Transfer Reaction – Mass Spectrometry (PTR-MS), which is the benchmark method for real-time monitoring of VOCs at very low concentrations. The results of these surveys were presented to the CSC. This proof of concept effort has resulted in South Coast AQMD to develop a PTR-MS mobile laboratory in order to conduct these measurements in-house (Attachment B)
- During the mobile survey conducted on June 25, 2019, instantaneous elevated concentrations of methyl mercaptan, an odorous compound that smells like rotten cabbage, were measured near the West Coast and Baker Commodities rendering facilities. Levels at the nearby residential communities were substantially lower (Attachment B)

Next steps

- Continue developing the PTR-MS mobile laboratory to conduct measurements of VOCs and odorous compounds near rendering facilities and in impacted communities
- Support Compliance and Enforcement investigations, where appropriate
- Investigate possible sources of odors west of Darling Delaware (Attachment B; Figure B-2)

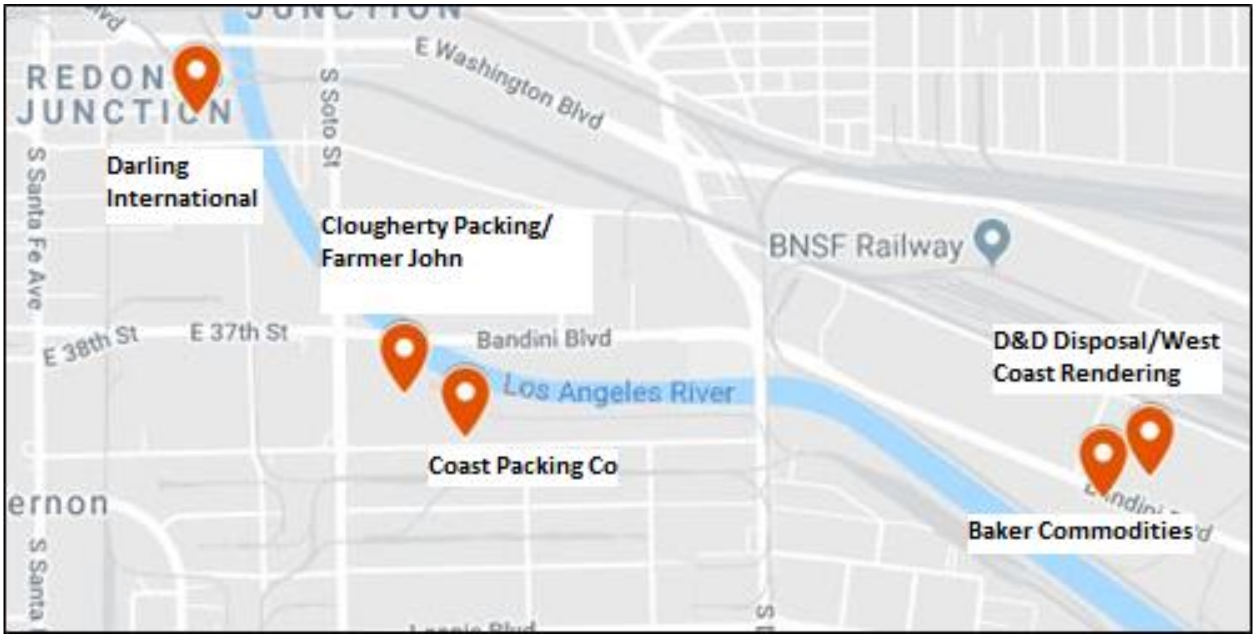
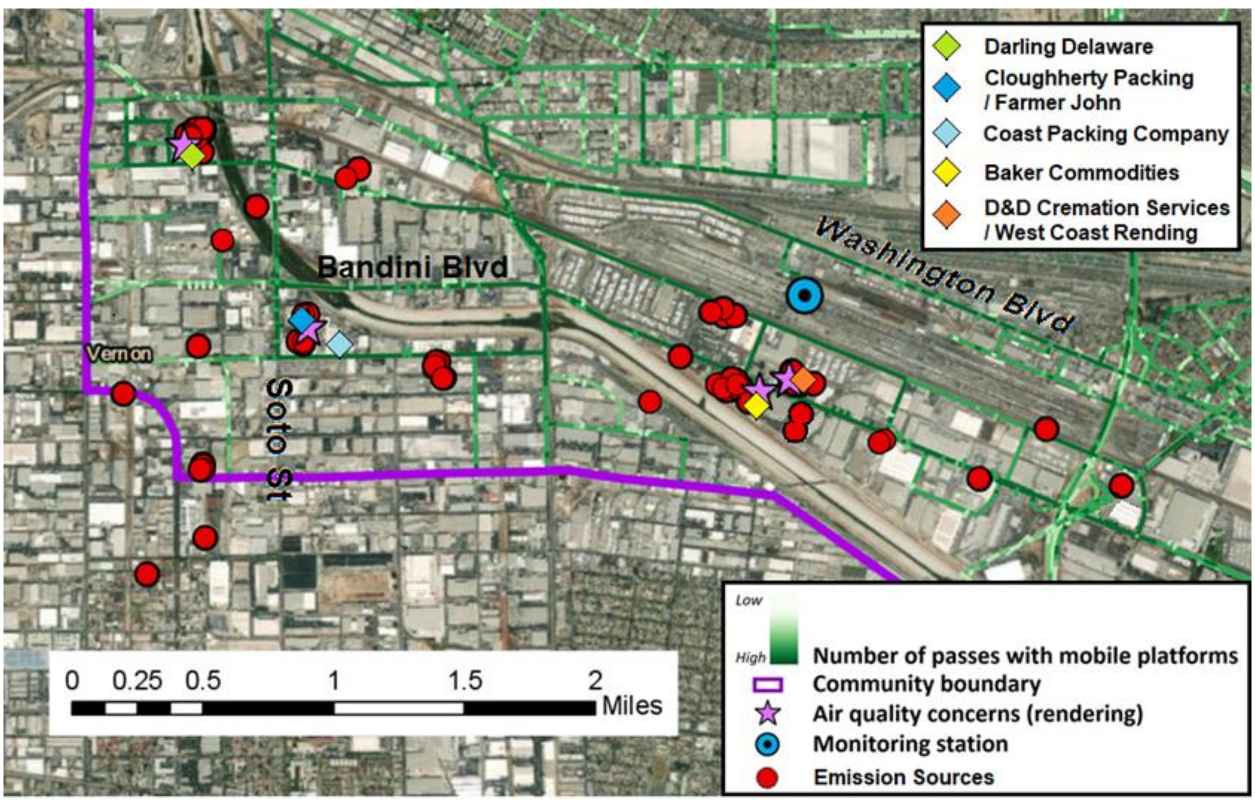


Figure 1. Map showing the locations of the five Rendering Facilities in the ELABHWC community

Attachment A

Dedicated flights were conducted by Aerospace Corporation between July 9 and 12, 2019. The dedicated wide-area airborne surveys covered central and east Los Angeles, including the entire East Los Angeles, Boyle Heights, West Commerce (ELABHWC) community. The bulk of the emissions observed during the central and east Los Angeles flights were predominantly ammonia and methane, with some ethene. Very few of the observed emissions coincided with the air quality priorities identified by the ELABHWC community steering committee (CSC). However, some ammonia, methane and in one case sulfur dioxide hotspots were close to the locations of the rendering facilities in the Vernon area (Figure A-1). These are listed in Table A-1, along with the emissions that were detected at each location. It is in the nature of airborne measurements that they can only represent "snapshots" of what would be detected on the ground. Furthermore, since all the data were acquired in the daytime, these observations are inevitably biased toward practices followed during normal working hours.



Attachment A-1. Aerospace Corporation aerial survey of rendering facilities on July 12, 2019. Aerial surveys can identify emission sources but cannot quantify emissions

Table A-1. Observed Emissions Near Rendering Facilities in the Vernon Area

Facility	Emissions Observed
Darling Delaware	Ammonia, Sulfur Dioxide
Farmer John / Coast Packing Co.	Ammonia
Baker Commodities	Ammonia, Methane
D&D Disposal / West Coast Rendering	Ammonia

Ammonia is an extremely common compound observed through all of airborne surveys, partly due to the high sensitivity and low minimum detection limits of the instrument used, and also because it is emitted by many natural and industrial sources, such as petroleum refining, some of the diesel exhaust control devices (e.g. selective catalytic reduction (SCR) systems for reducing oxides of nitrogen (NOx) emissions from the tailpipe exhaust), biomass burning, agriculture, animal husbandry, and rendering facilities. Methane is similarly common throughout the South Coast Air Basin due to the prevalence of oil and gas production and distribution in the region. Sulfur dioxide is a criteria pollutant and the South Coast Air Basin is in attainment of sulfur dioxide state and federal standards.

Attachment B

The main concerns raised by the CSC regarding rendering facilities in East Los Angeles, Boyle Heights, West Commerce (ELABHWC) relate to frequent strong and distinctive odors from their operations. In general, odors are mainly comprised of VOCs, some of which are classified as air toxics, as well as sulfuric compounds. South Coast AQMD has conducted mobile measurements for VOCs near each of the five rendering facilities in the ELABHWC community. For these surveys, the South Coast AQMD worked with Aerodyne Research LLC to conduct mobile measurements using a state-of-the-art Proton Transfer Reaction – Mass Spectrometry (PTR-MS) instrument, which is considered to be the benchmark method for simultaneous real-time monitoring of a wide range of trace-level VOCs. The results of these surveys were presented to the CSC. This proof of concept effort has resulted in South Coast AQMD developing a PTR-MS mobile laboratory to conduct these measurements in-house. A full report on the measurements performed by Aerodyne Research LLC is provided in Attachment C.

Figure B-1 shows the routes traversed by the Aerodyne Mobile Laboratory (AML) with respect to the location of the five rendering facilities identified by the CSC in the ELABHWC community (i.e., D&D Disposal/West Coast Rendering, Baker Commodities, Coast Packing Company, Clougherty Packing/Farmer Johns, and Darling Delaware). As shown in the figure, the mobile measurements were performed near and around (i.e., both upwind and downwind) of all these five facilities. This mobile monitoring campaign was performed in two different time intervals, between Friday June 14 and Wednesday, June 26, 2019; and between Saturday, November 2 and Thursday November 14, 2019.

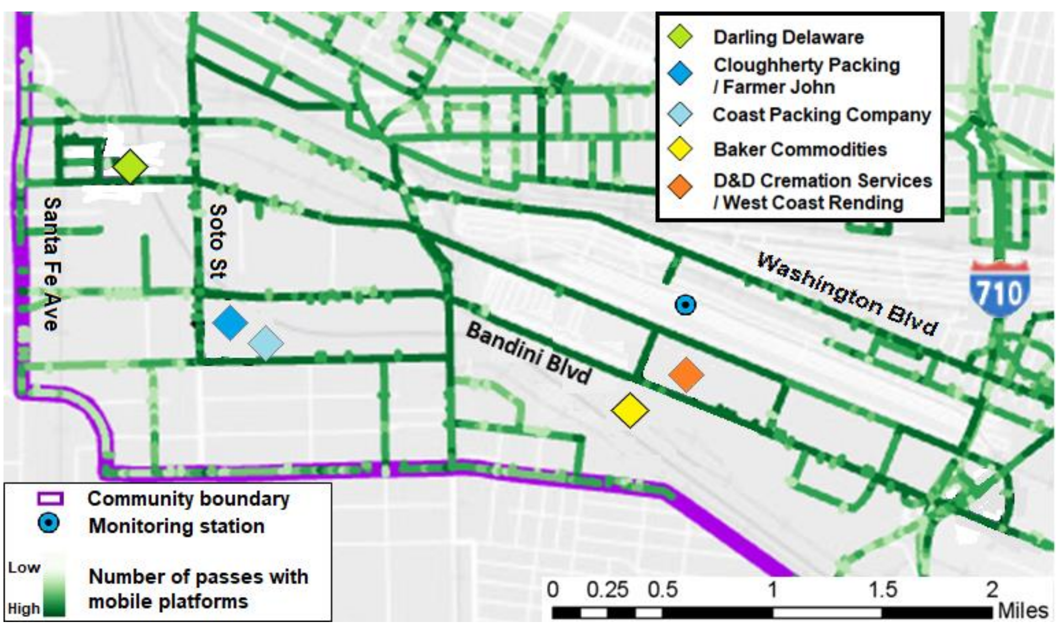


Figure B-1. Map of the ELABHWC community showing the number of passes conducted with mobile platform and the locations of the rendering facilities

A strong signal for odorous compounds was identified near all facilities. For example, persistent spikes were observed to the north of Baker Commodities and West Coast Rendering facilities, especially at the corner of 26th St. and S Indiana St. These signals were observed to have a strong sulfur signature, however, they also contained elevated terpenes, which generally have a strong, pleasant odor. Terpenes are frequently used in industrial deodorizers and cleaners, and their presence at high levels near the rendering facility suggests that scented products may already be in use for odor mitigation and/or cleaning. This is supported by visual evidence of these systems at facilities in the area.

Short term spikes in VOC concentrations were also observed near Farmer John and Coast Packing Company but shifts in wind conditions during this transect made it difficult to trace these emissions back to a specific facility. However, the plumes near these facilities are mainly characterized by the presence of sulfur compounds and no other unique VOC signatures were identified.

During two occasions in June 2019, Aerodyne Research LLC staff conducted measurements in the odor plumes while stationary and collected two cannister samples at two locations near Bandini Blvd. These were sent to the South Coast AQMD for chemical analysis using a standard Gas Chromatography (GC) method. Despite the measurement team reporting strong odors, results of the canister analysis indicated that none of the compounds detected by GC exceeded their odor thresholds. An important implication of this evaluation is that the standard GC analysis is not adequate in this situation, highlighting the importance of utilizing advanced techniques, such as mobile-based mass spectrometry.

This study demonstrated that the use of a well-equipped mobile laboratory is valuable for identifying pollution hotspots and their potential source in complex urban environments. Mobile surveys within a large community produce concentration maps which can help identify pollution hotspots and assess the extent of the community impact. Concurrent measurements of VOCs and wind speed/direction while "chasing" a pollution plume or driving around target facilities also enable locating the source(s) of emissions. Mobile monitoring can also result in detection of unexpected emission sources during mobile surveys of neighborhoods or during drives focused on other potential sources.

Aerodyne Research provided a comprehensive report on their air monitoring investigation which is included as Attachment C.

Attachment C

Application of Next Generation Air Monitoring Methods in the South Coast Air Basin

Prepared for

South Coast Air Quality Management District (SCAQMD)

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In association with:

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May 2020

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Executive Summary

Between Friday June 14th – Wednesday June 26th and Saturday November 2nd – Thursday November 14th, 2019, air quality measurements were conducted in the greater Los Angeles area, focusing on Carson, Wilmington, Long Beach, East Los Angeles, Muscoy, and San Bernardino. The Aerodyne Mobile Laboratory (AML) was equipped with state-of-the-art instrumentation to measure a broad range of atmospheric tracers, including volatile organic hydrocarbons (e.g. benzene, a carcinogen, and methane thiol, an odor concern), combustion species (e.g. CO_2 and CO from vehicle exhaust), particulate matter size, composition and mass, air toxic metals, and many others.

This campaign has further demonstrated that the use of a well-equipped mobile laboratory is valuable for emission studies in complex urban environments.

- Mobile surveys of a neighborhood can **quickly identify emissions hotspots**.
- Mobile laboratory measurements that include instrumentation to measure combustion markers, speciated volatile organic hydrocarbons, particulate matter, and other compounds of interest are ideal for urban or industrial areas with **numerous, varied and sometimes uncharacterized emission types**.
- **Unexpected emission sources** were encountered numerous times during neighborhood surveys or during drives focused on other potential sources. This type of "by-catch" increases the productivity and value of mobile laboratory studies.
- Mobile measurements under different wind conditions help narrow down source locations in congested areas.
- Stationary measurements included **sampling unique environments using adapted configurations** (e.g. extending sampling inlets into manholes and sewers – 'snorkeling').
- The live data display and mapping in the Aerodyne Mobile Laboratory allowed scientists to **regularly brief project management** on the latest observations during the filed campaign.
- The rapid preliminary data allowed for the campaign goals to be **flexible and adaptable**.

Introduction

The Aerodyne Mobile Laboratory (AML) is equipped with a suite of near-real-time, next-generation analytical equipment, capable of detecting a variety of important air pollutants, such as volatile organic compounds and air metal toxics. Therefore, the AML can also be used as effective screening tool to identify potential sources of emissions and to evaluate community exposure levels. Conducting surveys using filter sampling is labor-intensive and time-consuming, and allows for neither continuous monitoring, dense spatial coverage, nor effective screening. Therefore, SCAQMD has a pressing need to implement an alternative approach to screening, particularly for toxic metals in the air. Recent advancements in real-time analytical techniques offer such promise. This study was therefore targeted at making significant advancements in monitoring toxic metals and volatile organic compounds in communities located near various industries and businesses.

Preparation for this study required obtaining and integrating several new instruments. Before arriving at SCAQMD for the June campaign, the mobile laboratory drove to Cooper Environmental Services headquarters in Beaverton, Oregon for installation of a Xact® 625i (energy dispersive X-ray fluorescence technique) rented for this project. Aerodyne employees were trained on the unit which had been specially adapted to report many airborne metals and their concentrations every 5 minutes as opposed to 15 minutes (fastest measurement previously available). For the November campaign, a similar unit was borrowed from SCAQMD. A small portable sensor from AethLabs (San Francisco, CA), the microAeth® MA 350, measures black carbon (BC) at 1 Hz and was also borrowed from SCAQMD during the June campaign. Data from this sensor replaced that from a Multi-Angle Absorption Photometer (MAAP) on-board (data delivered during the campaign). Another new addition, the Vocus 2R PTR-TOF, measured volatile organic compounds (VOCs) in air. This instrument, recently developed, boasts low detection limits and high resolving power. All these additions and changes demonstrate the flexibility of this platform to successfully incorporate new instruments and equipment.

The Aerodyne mobile laboratory was deployed between Friday June 14th – Wednesday June 26th and Saturday November 2nd – Thursday November 14th. Measurements were taken in the greater Los Angeles area, focusing on Carson, Wilmington, Long Beach, East Los Angeles, Muscoy, and San Bernardino. Throughout this report, individual facilities are named or drawn on a map. It is important to note that this does not indicate that they are the source of a given emission unless specifically described as such.

Experimental

Platform overview

The Aerodyne Mobile Laboratory is an instrumented box truck (Figure 1) designed to support a flexible deployment of research-grade air monitoring equipment. A schematic in Figure 2 shows the instrumentation used during this field campaign.

Figure 1. The Aerodyne Mobile Lab parked at SCAQMD in Diamond Bar, CA.

Ambient air is continuously drawn through the inlets at the front of the vehicle, which extend out on booms mounted to the roof. Every 15 minutes, clean air was delivered in excess of the intake flow for three of the inlets: the trace-gas inlet (blue, Figure 2) and the VOC inlets (purple and green, Figure 2). The air was either dry ultra-zero air or humidity-matched air from an Aadco ZA30 zero-air generator (Cleves, OH), respectively. These gas additions served to spectroscopically background select laser-based instruments, and to check zero values for the other instruments. The other inlets were dedicated to particulate matter measurements (red, Figure 2), and were manually checked for zero levels using a removable filter on the inlet tip.

Meteorological conditions and GPS-based positioning were measured on the rooftop. A Hemisphere (V103) GPS Compass (Scottsdale, AZ) was operated in conjunction with an RM Young 2D (Traverse City, MI) anemometer to determine wind speed and direction and to map vehicle location, speed and bearing during measurements. True wind was determined by vector subtraction of the mobile laboratory speed from the raw measured wind speed.

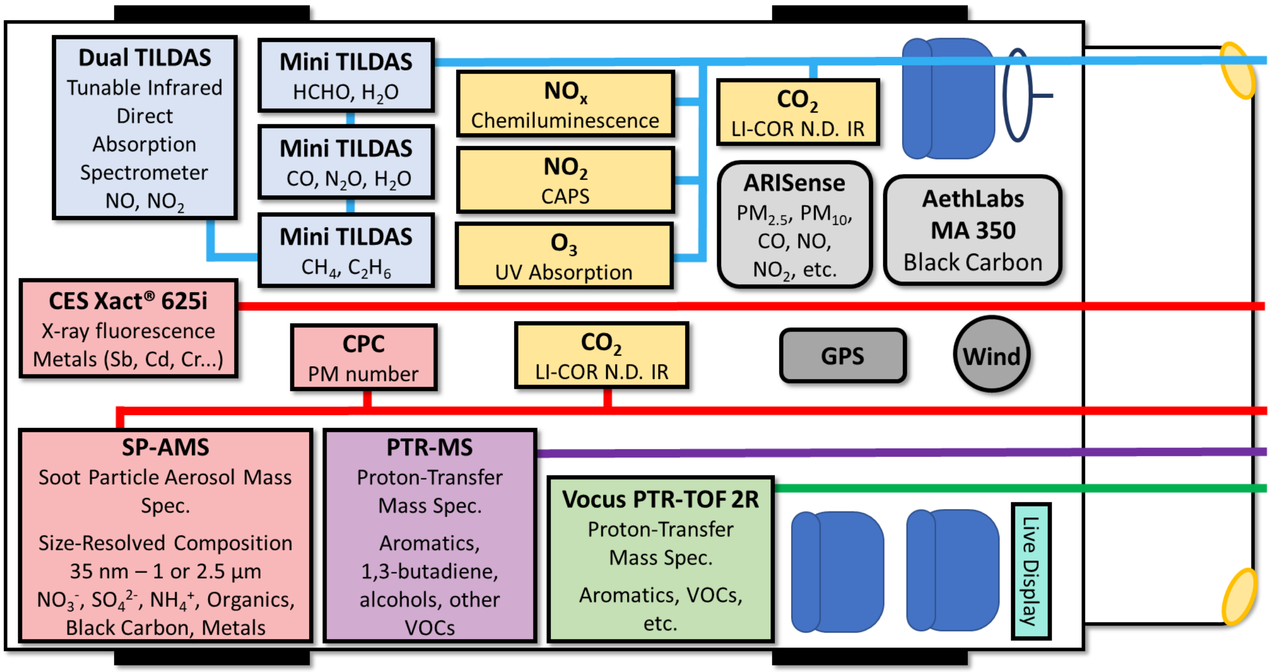

Figure 2. Schematic of the Aerodyne Mobile Laboratory during the 2019 SCAQMD field campaigns. Particulate matter instrumentation (red inlet) include condensation particle counter (CPC) and the soot particle aerosol mass spectrometer (SP-AMS). Volatile organic compound instrumentation (purple and green inlets) includes two proton transfer mass spectrometers (PTR-MS and Vocus 2R PTR-TOF). Trace gas instrumentation (blue background) includes mini or dual tunable infrared direct absorption spectrometers (TILDAS) as well as a few other commercial instruments (yellow background), all on the blue inlet. Roof-mounted sensors (grey background) include global positioning system (GPS), wind, AethLabs MA350, and the ARISense sensor.

Inside the AML, air in the trace-gas inlet is sampled by a LI-COR 6262 for CO_2 (Lincoln, NE), an Aerodyne cavity attenuated phase shift (CAPS) sensor equipped with an ozone generator for total nitrogen oxides (NOx, November only), and a 2BTech Model 205 ozone (O_3) monitor (Boulder, CO). Trace-gas monitors employing Tunable Infrared Laser Direct Absorption Spectroscopy (TILDAS) from Aerodyne Research, Inc. performed gas phase measurements of the ambient air (McManus et al., 2015). Three single laser "mini" instruments and one dual-laser instrument measured 1) formaldehyde and water (HCHO, H_2O), 2) nitrous oxide, carbon monoxide and water (N_2O, CO, and H_2O); 3) ethane and methane (C_2H_6 and CH_4); and 4) nitrogen oxide and nitrogen dioxide (NO, NO_2, June only). A mini-TILDAS measured hydrogen cyanide (HCN) and acetylene (ethyne, C_2H_2) in November. The TILDAS instruments were operated in series at pressures between 30-50 Torr, with an upstream pressure controller managing flow from a downstream scroll pump (Agilent TriScroll TM 600 - Santa Clara, CA). All TILDAS instruments were spectroscopically zeroed, except for the N_2O-CO monitor, due to residual CO present in ultra-zero air. Instrument calibrations for gas-phase species were performed by overblow of the inlet with a quantitatively blended mix of ppm-level calibration standards with a diluent (ultra-zero air or ZAG air).

A proton-transfer reaction mass spectrometer (PTR-MS) with quadrupole MS, operated in NO^+ mode and measured from the VOC inlet (purple, Figure 2) during only the June campaign. In this mode, the instrument is also called NOMS. It measured methanol, acetaldehyde, acetone and benzene. Instrument calibrations for gas-phase species were performed by overblow of the inlet with a quantitatively blended mix of ppm-level calibration standards with a diluent (ultra-zero air or ZAG air).

A time-of-flight based proton-transfer reaction mass spectrometer (Vocus 2R PTR-TOF) measured from another VOC inlet (purple, Figure 2) and measured VOCs including benzene, toluene, xylenes (C2-benzenes), acetone. Select sulfur compounds were also measured including methane thiol (CH_3SH), the sum of ethane thiol and dimethyl sulfide, dimethyl disulfide. A list of species is included in the Quality Assurance spreadsheet that accompanies the data.

An Aerodyne soot particle aerosol mass spectrometer (SP-AMS) measured particulate matter mass (PM_m μm m^{-3}) and composition. It was equipped with a high-resolution time-of-flight mass spectrometer (HR-TOF). Particulate matter sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), chloride (Cl^-) and organic carbon ("Org") were measured with this instrument. The addition of the SP laser allowed for measuring both black carbon (BC) and metals. The metals monitored with this instrument include chromium (Cr), cadmium (Cd), aluminum (Al), Tin (Sn), and many others. The full list of output species is available in Appendix B. This instrument has an internal size cutoff (< 2.5 μm throughout the campaign) and the inlet sampled from a < 2.5 μm cyclone.

An ambient multi-metal monitor from Cooper Environmental Services (Beaverton, Oregon) called the Xact® 625i was used in both campaigns. It uses an energy dispersive X-ray fluorescence technique to analyze and detect metal in PM deposited on Teflon filter tape. This instrument was set up in a custom 5-minute sampling mode as opposed to typical longer-term sampling modes (15, 30, 60 minutes and longer). This instrument used a dedicated total suspended particle inlet with a sample flow rate at 16.7 lpm. Racks were installed to house and secure the instrument while mobile.

A condensation particle counter (CPC) measured particulate matter number (PM_n, # cm^{-3}). An AethLabs microAeth® MA 350 measured black carbon (UV-IR, μg m^{-3}), either from the roof-top or attic area (with an inlet run out the bulkheads in front). An ARISense mounted to the vehicle rooftop measured particulate matter number in 16 size bins between 0.4 –16 μm with an optical particle counter (Alphasense model OPC-N2). Subsequent analysis provided measures of integrated size-dependent particulate matter mass, like PM_2 and PM_{10} (see Appendix B). Other measured quantities include solar insolation, wind, RH, and duplicate measurements of CO, NO and NO_2. The unit was mounted flat against the roofline ("up" points forward) to prevent exceeding vehicle height restrictions, and so this unit's wind measurements were not used, and the solar insolation used only qualitatively.

Real-time data was logged and displayed on monitors in the AML, allowing scientists to rapidly detect and follow plumes of interest. Custom software was used to download, display, and update maps of the area, which were underlaid on live data graphs. Notes were recorded on the same computer and the observer defined periods of trace-gas data showing enhancements above background (plumes) while in the field.

Data Access

Aerodyne Research, Inc. visited the South Coast Air Basin for two campaigns in 2019:

June: 06/14/2019 23:00 to 06/26/2019 14:30 UTC
November: 11/02/2019 00:00 to 11/14/2019 21:00 UTC

Data was taken in the greater Los Angeles area. Two time-segments are used throughout, one each for the June and November campaign. Data reported here includes only mobile data taken 30 meters or more away from the overnight parking location at SCAQMD headquarters. There are two reasons for pairing down the data in this way:

1. Some instruments were not collecting data overnight, including particulate matter speciation data from the Aerosol Mass Spectrometer (AMS) and airborne metal data from the Cooper Xact® 625i (Cooper Environmental Services, Beaverton, OR) and the Vocus.
2. Excluding overnight data allows for the creation of comma-separated-value (.csv) files that have few enough columns to be opened in Microsoft Excel. This makes these data files easily accessible to future researchers and collaborators.

Data is stored on a shared drive specific to this project. Contact for access:

tyacovitch@aerodyne.com

Comma-separated-value files (.txt) are named as follows, where "yyyymmdd" indicates the year, month, and day of the file revision.

Aerodyne_SCAQMD2019_November_yyyymmdd.txt
Aerodyne_SCAQMD2019_June_yyyymmdd.txt

Each file starts with a column for datetime in UTC and Local time. Null data is reported as blank. All data columns are described below. Data columns begin with SS_, indicating that the data has been interpolated onto the 1-second master time for the campaign.

A spreadsheet containing data QA notes is included. The table is also reproduced below. For additional details on instruments in use, definitions of analysis product data, and QA steps taken, see Appendix B from Aerodyne's 2018 CrVI project, "Application of Next Generation Air Monitoring Methods in the South Coast Air Basin".

The full .h5 files for the AMS instrument, which was present on the AML for the December campaign, has been mailed to SCAQMD on a USB key. The full Cooper Xact® 625i dataset for November has also been delivered to SCAQMD.

Table 1. List of data vectors and quality assurance (QA) notes

Column Name	Long Name	Units	Instrument	Note	Data QA Note (b.)
SS_datetimeUTC	Universal Coordinated Time	Universal Coordinated Time			Data reported only when truck was >30 m away from SCAQMD parking spot.
SS_LocalTime	Local Time	PDT in June; PST in November		PDT = UTC - 7h; PST = UTC - 8h	
SS_Latitude	Latitude	decimal degrees	HemiRover Vector v103 GPS Compass		

Column Name	Long Name	Units	Instrument	Note	Data QA Note (b.)
SS_Longitude	Longitude	decimal degrees	HemiRover Vector v103 GPS Compass		
SS_Easting	Universal Transverse Mercador Easting	meters	HemiRover Vector v103 GPS Compass		
SS_Northing	Universal Transverse Mercador Northing	meters	HemiRover Vector v103 GPS Compass		
SS_Zone	Universal Transverse Mercador Zone	meters	HemiRover Vector v103 GPS Compass		
SS_Elevation_m	Truck Elevation	meters	HemiRover Vector v103 GPS Compass		
SS_truckSpeed_kmph	Truck Speed	kmph	HemiRover Vector v103 GPS Compass		
SS_truckHeading	Truck Heading	degrees clockwise from true North	HemiRover Vector v103 GPS Compass	Orientation of the truck axis	
SS_SolarElevAngle	Solar Elevation Angle	azimuthal degrees	Calculated based on truck position		
SS_wind_speed_metersPerSecond	Wind Speed	meters per second	RM Young 2D Anemometer	Unreliable at high truck speeds	
SS_wind_dir_degrees	Wind Direction	degrees clockwise from true North	RM Young 2D Anemometer	Unreliable at high truck speeds	
SS_wind_E_metersPerSecond	East component of wind	meters per second	RM Young 2D Anemometer	Unreliable at high truck speeds	
SS_wind_N_metersPerSecond	North component of wind	meters per second	RM Young 2D Anemometer	Unreliable at high truck speeds	
SS_Temperature_C	Outdoor temperature	meters per second	RM Young 3D Sonic Anemometer		

Column Name	Long Name	Units	Instrument	Note	Data QA Note (b.)
SS_Snorkel	Snorkeling Flag	unitless		0 is ambient sampling; 1 is snorkeling through an extended inlet tube	
SS_strictBackgroundMask	Strict Background Mask	unitless	Calculated based on measured CO	1 is sampling that is not affected by sharp exhaust spikes; NaN (blank data) is affected by exhaust	
SS_CO2_ppm	Carbon dioxide	ppm	LI-COR 6262	Ambient humidity	Calibrated
SS_CO	Carbon monoxide	ppb	TILDAS	Ambient humidity	Calibration factor close to 1 and within uncertainty of tank, so no calibration factor applied
SS_CO_background	Carbon monoxide background	ppb	Calculated based on measured CO	Ambient humidity	Calibration factor close to 1 and within uncertainty of tank, so no calibration factor applied
SS_N2O	Nitrous oxide	ppb	TILDAS	Ambient humidity	No calibration factor applied. Ambient concentrations agree with NOAA background concentrations for 2019 34-degree latitude
SS_NOx	Nitrogen oxides	ppb	TILDAS or CAPS-NO2	In June, NOx is sum of NO and NO2. In December, NOx is direct measurement of NOx after reaction with excess Ozone. Ambient humidity	November NOx data requires advanced QA to diagnose problem with ozone generator
SS_NO	Nitric oxide	ppb	TILDAS	No data collected in November	N/A
SS_NO2	Nitrogen dioxide	ppb	TILDAS	TILDAS in June; CAPS-NO2 in November.	No data reported
SS_H2O	Water vapor	ppb	TILDAS	Ambient humidity	No calibration factor applied
SS_O3	Ozone	ppb	TILDAS	Ambient humidity	No calibration factor applied
SS_CH4	Methane	ppb	TILDAS	Ambient humidity	Calibrated
SS_C2H6	Ethane	ppb	TILDAS	Ambient humidity	Calibrated
SS_HCN	Hydrogen cyanide	ppb	TILDAS	Ambient humidity	Calibrated
SS_C2H2	Acetylene (ethyne)	ppb	TILDAS	Ambient humidity	Calibrated
SS_HCHO	Formaldehyde	ppb	TILDAS	Ambient humidity	No calibration factor applied

Column Name	Long Name	Units	Instrument	Note	Data QA Note (b.)
SS_benzene	Benzene	ppb	Vocus (a.)		Calibrated
SS_toluene	Toluene	ppb	Vocus (a.)		Estimated response (c.)
SS_C2benzene	Sum of xylene isomers (aka C8-aromatics)	ppb	Vocus (a.)		Calibrated
SS_C3benzene	Sum of C9-aromatics	ppb	Vocus (a.)		Calibrated
SS_CH3SH	Methane thiol (methyl mercaptan)	ppb	Vocus (a.)		Estimated response (c.)
SS_acetone	Acetone	ppb	Vocus (a.)		Calibrated as acetone
SS_acetaldehyde	Acetaldehyde	ppb	Vocus (a.)		Calibrated as acetaldehyde
SS_MEK	Methyl ethyl ketone	ppb	Vocus (a.)		Calibrated as MEK
SS_isoprene	Isoprene	ppb	Vocus (a.)		Calibrated as isoprene
SS_monoTerpenes	Sum of monoterpenes	ppb	Vocus (a.)	Exact mass 137.132	Calibrated as alpha-pinene
SS_C2H5O2	Acetic acid, propanol and other isomers	ppb	Vocus (a.)	Exact mass 61.028	Estimated response (c.)
SS_C7H15O	Heptanal and other isomers	ppb	Vocus (a.)	Exact mass 115.112	Estimated response (c.)
SS_DMDS	Dimethyl disulfide, measured via ion C2H7S2+	ppb	Vocus (a.)	Exact mass 94.998	Estimated response (c.) using rate constant from Cappelin[1] and formula from Seikimoto[2]
SS_C2H7S	Sum of dimethyl sulfide and ethane thiol	ppb	Vocus (a.)	Exact mass 63.026	Estimated response (c.), calibrated as DMS (Sekimoto[2])
SS_C4H9S	Tetrahydrothiophene and other isomers	ppb	Vocus (a.)	Exact mass 89.042	Estimated response (c.) using rate constant for C4 thiols and sulfides (Sekimoto)
a. Vocus relies on mass-based detection. Interference from structural isomers are possible. See the PTR Spreadsheet. https://docs.google.com/spreadsheets/d/108MzOYtjequJHZ2N_fth1yFM7XnlGzOlQ7tPkvK5FHQ/edit#gid=0					
b. For additional QA details, see QA document from 2018 Campaign					
c. Estimated response does not account for fragmentation.					

References

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Results, Discussion, Conclusions

Rendering Plants

Introduction

Rendering facilities process animal byproduct from slaughtering operations. These facilities grind, cook and separate animal carcasses into product streams including different grades of fats (for human or animal consumption), protein meals, fertilizer, and biodiesel feedstocks. Alternatives to rendering are not generally feasible on a large scale (e.g. landfill, incineration, composting, etc.), and so rendering facilities play an important role in the supply chain for meat.

In 2017, new odor regulations targeting rendering facilities were passed.[1] The rendering facilities on Bandini Boulevard, including West Coast Rendering and Baker Commodities are facilities subject to these new rules.

Previous research on rendering plant emissions have identified numerous volatile organic chemicals (VOCs).[2,3] These VOCs appear in differing concentrations downwind of different parts of the facility and include numerous malodorous compounds. The VOCs that have been found in highest concentrations include ammonia, acetic acid, acetone, aldehydes and ketones, and ethanol.[2] The most odorous VOCs identified include volatile fatty acids, aldehydes and sulfur compounds (dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide).[2,3] In this report, we also identify methane thiol (aka methyl mercaptan) as a key odor compound.

Odor is extremely subjective: each person will have a different perception of what smells "bad". Furthermore, the concentrations that are detectable by the human nose vary by orders of magnitude depending on the compound. Methane thiol is detectable at 70 parts-per-trillion (ppt); ethane thiol at even smaller concentrations (8.7 ppt).[4] Numerous other compounds can be detected at even lower concentrations. Acetone needs to be present in about a million times larger concentrations than methane thiol for it to be detected by smell (42 ppm).[4]

The concentration measurements presented in this report will not be able to completely characterize odors for these reasons and more. Certain malodorous compounds may be present that cannot be detected or have not yet been identified in the raw dataset. The combined effects of multiple compounds on the final perceived odor is also unknown.

The Aerodyne Mobile Laboratory (AML) visited an area around Bandini Blvd that is home to numerous animal rendering facilities and associated industries. Animal processing companies located in this area include Baker Commodities, Central Valley Hide and West Coast Rendering.

Other industries are in this area of Bandini Blvd, including Rehrig Pacific, a plastics manufacturer, and Republic Services Innovative Waste Control Transfer Station, to the north of Bandini Blvd. Other rendering facilities were also visited, including Farmer John and Darling Delaware.

The measurements cover the dates and approximate times below. Measurements in June are the focus of this report, but measurements in November were also done.

- 6/21/19 19:24:06 6/21/19 19:28:21 Darling Delaware
- 6/21/19 19:32:37 6/21/19 19:36:40 Farmer John
- 6/21/19 19:43:03 6/21/19 19:59:15 Darling Delaware
- 6/21/19 20:22:16 6/21/19 20:51:16 Bandini Blvd.
- 11/4/19 17:00 11/4/19 19:30

Instrumentation Notes

The Vocus 2R PTR-TOF instrument continuously sampled the air as the AML drove near the plants, and chemical identification of compounds is done live by mass spectrometry. This contrasts with previous measurements, which used extractive sampling (canisters or Nalophan bags) and analysis via gas chromatography mass spectrometry (GC-MS) and other laboratory methods.

The AML does not have measurements of most saturated aliphatic hydrocarbons, one the classes of compounds expected to contribute to odor. Another such species, ammonia (NH_3), was measured only during the summer campaign, but with a high limit of detection.

One challenge in the chemical identification of species measured with the Vocus is that structural isomers are indistinguishable via proton transfer mass spectrometry (PTR-MS, of which Vocus is a variant). For example, the $C_4H_9O^+$ ion could be any combination of butanal, 2- or 3-butanone, or 2- or 3- methyl propanal. As another example, ethane thiol, CH_3CH_2SH, and dimethyl sulfide, CH_3SCH_3, are both detected as $C_2H_6S(H^+)$, or, simply, $C_2H_7S^+$. In some cases, fragmentation patterns can help disambiguate chemical identification. A listing of some identified species by PTR-MS in the literature is available online.[5,6] This list is not exhaustive, but can help with identification of species and of their structural isomers.

Response factors for selected compounds not included in the calibration tank are determined based on their literature or calculated rate constants with the hydronium reagent ion (kCap).[7] The ionization reaction rate curve (Sensitivity in cps/ppb vs kCap) for calibration tank compounds is calculated to have a slope of 1437.5. A table of response factors for sulfur-containing compounds is shown below. This table shows that a 0.07 ppb methane thiol signal would correspond to approximately 176 counts-per-second (cps). These response factors do not account for fragmentation or isomers.

Table 2. Response factors for selected sulfur compounds.

Formula	m/z (amu)	Chemical Name	k_cap	Response Factor (cps/ppb)	Ref
CH_5S	49.011	Methane thiol (methyl mercaptan)	1.75	2516	Sekimoto[7]
C_2H_7S	63.026	Ethane thiol (ethyl mercaptan) and Dimethyl sulfide (DMS)	2.00	2875	Sekimoto[7]
$C_2H_7S_2$	94.998	Dimethyl disulfide (DMDS)	2.39	3436	Sekimoto[7] and Cappellin[8]

Maps are displayed with units of counts-per-second (cps). Table 2 lists the response factor which can be used to convert from counts-per-second to parts-per-billion (ppb). These response factors do not include subtle variations in instrument response over the course of the campaign, which is expected to be less than 10%.

On two occasions in June, the AML sat stationary in odor plumes and collected canister samples. These were sent to SCAQMD for analysis. 1917737-01 (Sampled: 6/25/2019 20:36) and 1917738-01 (Sampled: 6/25/2019 21:03). This canister analysis is described in the results section.

Odor and Measured Concentration

Sensory perception of noxious odors is recognized as being highly subjective due to individual sensitivity. The wide range of human sensitivities makes identifying and quantifying the specific compound or compounds associated with the odor highly challenging. Noxious odors can be classified into two broad categories: One is the presence of trace levels of a particularly odorous compound such as one of the mercaptans used intentionally to odorize natural gas. The second category is when an excess of organics is present that it simply overwhelms the sensory system. In this latter category there may or may not be any single component responsible and reducing the total organic loading is most likely the best mitigation strategy.

Sulfur compounds are typically the source of most malodors, but amines and low molecular weight aldehydes and carboxylic acids also present offensive odors. In a survey such as this it is appropriate to use the sulfur compounds as a metric for identifying and characterizing areas possessing an odor problem. Methyl mercaptan or methane thiol (CH_3SH, detected via the ion CH_5S^+) was observed at most of the target sites and will serve as a tracer for defining the sources (locations) with probable odor problems. Methyl mercaptan has a low threshold sensitivity of only 70 ppt and this value will be used to define the locales deemed as problem areas. Within these regions the chemical composition will be explored to find signatures that appear to be unique to a specific source. The fingerprint only helps distinguish or differentiate sources and may or may not pertain to defining the nature of the odor. The composition can be interrogated more thoroughly through examining the full mass spectrum obtained during the time periods defined by the fingerprint.

Table 3. Odor notes for selected compounds. [a.]

Chemical compound	Protonated chemical formula	Odor note [a.]	Odor detection threshold (ppb)[4]
Methane thiol	CH_5S+	Rotten cabbage	0.0700
Ethane thiol	C_2H_7S+	Odorized natural gas, garlic or skunk-like	0.0087
Dimethyl sulfide (DMS)	$C_2H_7S_2+$	Unpleasant cabbage-like	3.0
Dimethyl disulfide (DMDS)	$C_2H_7S_3+$	Unpleasant garlic-like odor	2.2
Ammonia	NH_4+ (no data collected)	Pungent	1500
Acetone	C_3H_7O+	Nail polish remover	42000
Butanal	C_4H_9O+	Pungent aldehyde	0.67
Pentanal	$C_5H_{11}O+$	Pungent, acrid	0.41
Hexanal		Fresh-cut grass	
Isobutyraldehyde (2-methyl propanal)	C_4H_9O+	Pungent straw-like	0.35
2-butanone	C_4H_9O+	Sharp, sweet	
2-heptanone		Banana, fruity	
3-methyl butanal		Apple-like, suffocating	
2-methyl butanal		Musty, chocolate	
Benzaldehyde		Almond	
Xylenes		Sweet	

a. Odor notes from Wikipedia and theGoodScentsCompany.com

A challenge that is presented in this approach is when neighboring facilities are actively employing deodorizing strategies. We noted significant plumes of terpenes (α-pinene or limonene) downwind of the West Coast rendering facilities. α-pinene is normally associated with emissions from trees (conifers), but α-pinene, limonene and other terpenes are routinely used in lemon, pine, and other scented products. Their presence at such high quantities at the rendering facility suggests that scented products may already be in use for odor mitigation and/or cleaning. Indeed, the measurement team observed containers that may have contained industrial air freshener at facilities near Bandini Blvd. We note that these products may also be in use by nearby businesses to mitigate odor from their neighbors.

Time series investigation reveals that in June, the AML visited several facilities where brief enhancements in methane thiol were observed. The accompanying map illustrates the methyl mercaptan signature for June 2019 measurements, where the yellow coloration indicates when the concentration exceeded ~ 70 ppt.

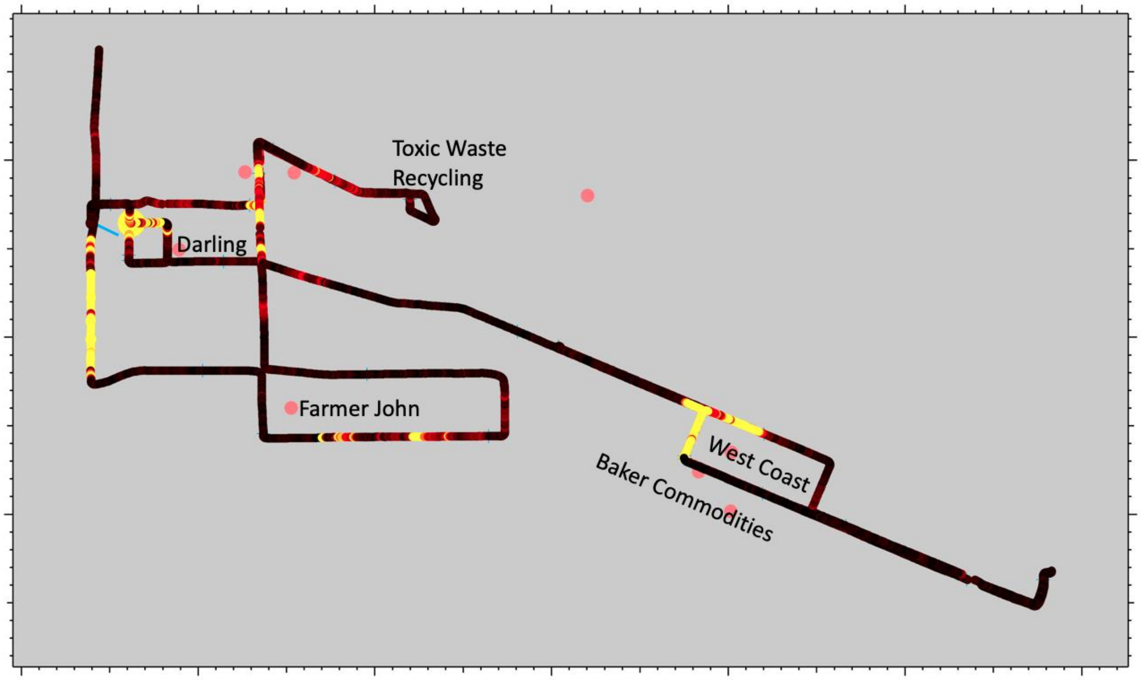

Figure 1. Methane thiol concentrations in Vernon, 6/21/2019. Yellow indicates concentrations exceeding ~70 ppt. Only select facilities are listed, but others are present.

The most complicated area is that surrounding the Darling Delaware facility where at least 3 different source profiles can be identified. The repeated transect around the block by Darling reveals two distinct plumes identified by differences in the relative amounts of methyl mercaptan and dimethyldisulfide. The underlying structure of the C_4H_9O and $C_5H_{11}O$ signals also is observed to by highly correlated with the methyl mercaptan signal. These same features exist in the plume to the southwest of Darling and are suggestive they from the same source. The plume to the east of Darling is clearly different as here there is signature from C_3O (identity unknown) that is highly correlated with this methyl mercaptan source. Toxic Waste Recycling bears no sulfur signature but is represented by the large TIC signal at ~ 8:12 PM. The total VOC loading exceeds ~ 200 ppb a level which can clearly be detected as offensive. The Farmer John plumes (7:30-7:40) only appear to have sulfur compounds as no other unique signature has yet to be identified. The Bandini Blvd area, which includes West Coast Rendering, Baker Commodities, and numerous other facilities, shows a strong persistent sulfur signature, but the composition is complicated by the presence of a deodorization system.

The benzene signal (C_6H_7) is included to identify the TIC plumes associated with vehicle exhaust that can be ignored as potential odor plumes.

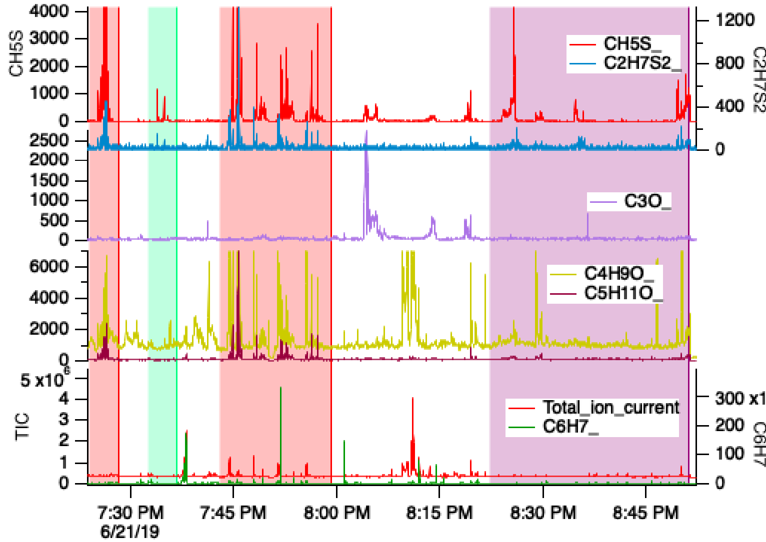

Figure 2. Selected VOCs detected with the Vocus on 6/21/2019. All concentrations reported in counts per second. Scales are zoomed in vertically. Total ion current (TIC) is also reported. Shaded areas correspond to times spent sampling near facilities: West Coast Refining and Baker Commodities (purple); Farmer John (green); Darling Delaware (red)

Subsequent sections will zoom in on the plumes from rendering facilities.

Bandini Blvd. Facilities

Baker Commodities is a facility south of Bandini Blvd. The map below outlines the area in question. Google Street-View images from points 1-3 are shown.

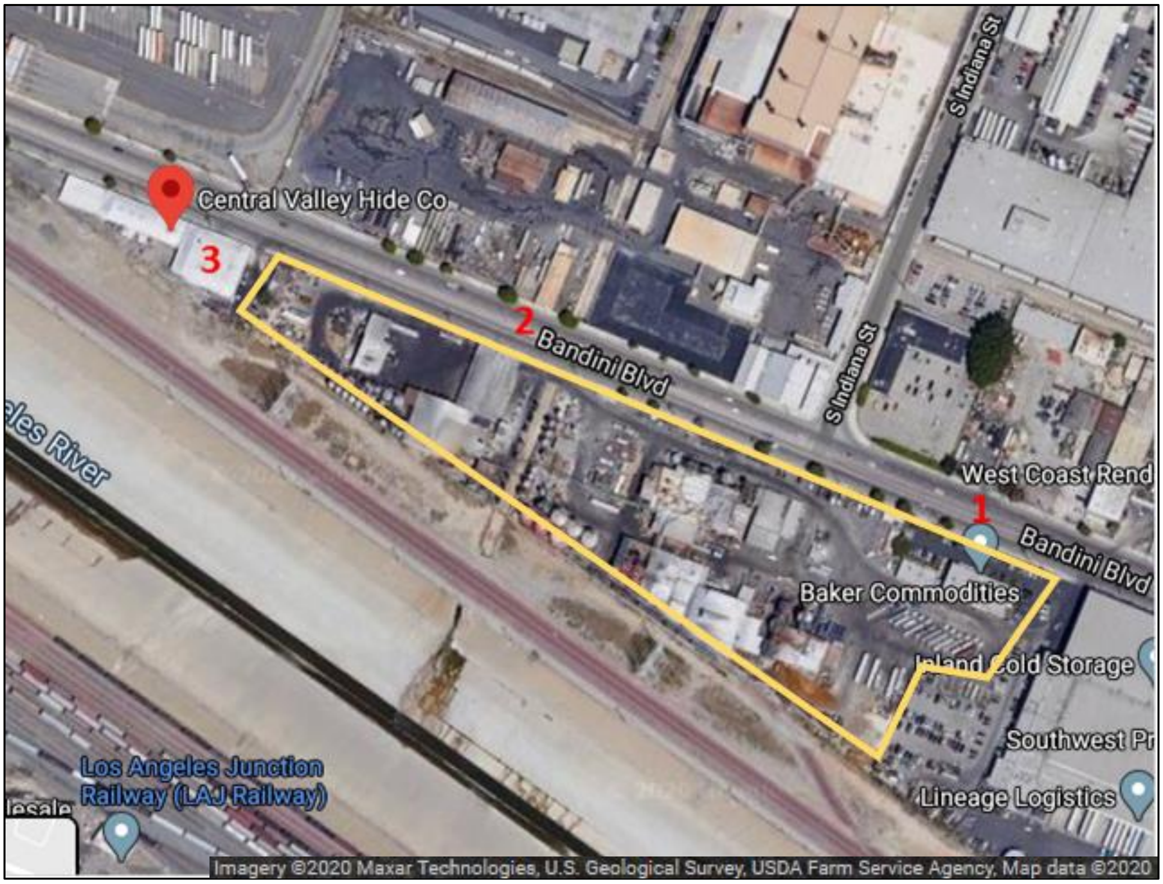

Figure 3. Map of Baker Commodities, south of Bandini Blvd (yellow polygon). Two other nearby animal processing facilities are also noted: Central Valley Hide (west) and West Coast Rendering (north of Bandini Blvd).

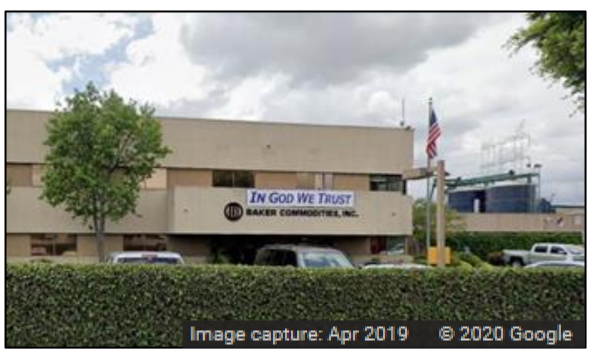

Figure 4. At Point 1, a Baker Commodities office building.

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Figure 5. At point 2, a truck with a Baker Commodities logo

Figure 6. And at Point 3, we see the border between Baker commodities and Central Valley Hide.

Other industries are in this area of Bandini Blvd, including Rehrig Pacific, a plastics manufacturer, and Republic Services Innovative Waste Control, to the north of Bandini Blvd.

West Coast Rendering is located to the north of Bandini Blvd.

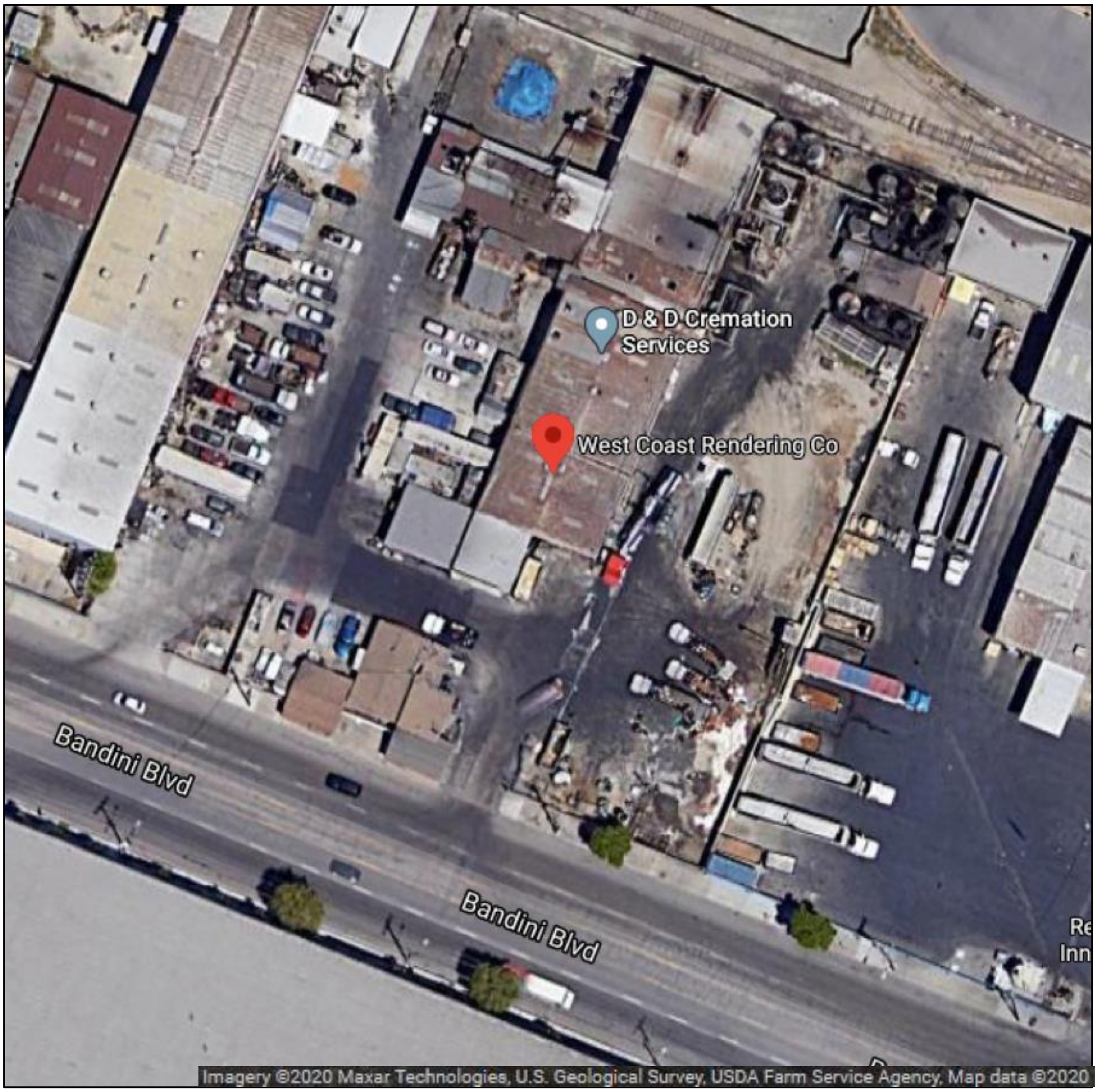

Figure 7. Map of the West Coast Rendering Co. on Bandini Blvd.

In contrast with Darling Delaware, West Coast Rendering Co. appears to have more open-air staging areas. (Bottom right of map). This agrees with a newspaper article picture showing animal carcasses piled in a parking lot.

Figure 8. Rendering facility image from the Los Angeles Times: "Vernon-area animal rendering facilities, including this one on Bandini Boulevard, must adhere to new rules […] aimed at reducing foul odors." (*Al Seib / Los Angeles Times*).

Figure 9 shows two main methane thiol measurements, one on E 26th St, north West Coast Rendering, and one on S Indiana St, just before Bandini Blvd, near Baker Commodities.

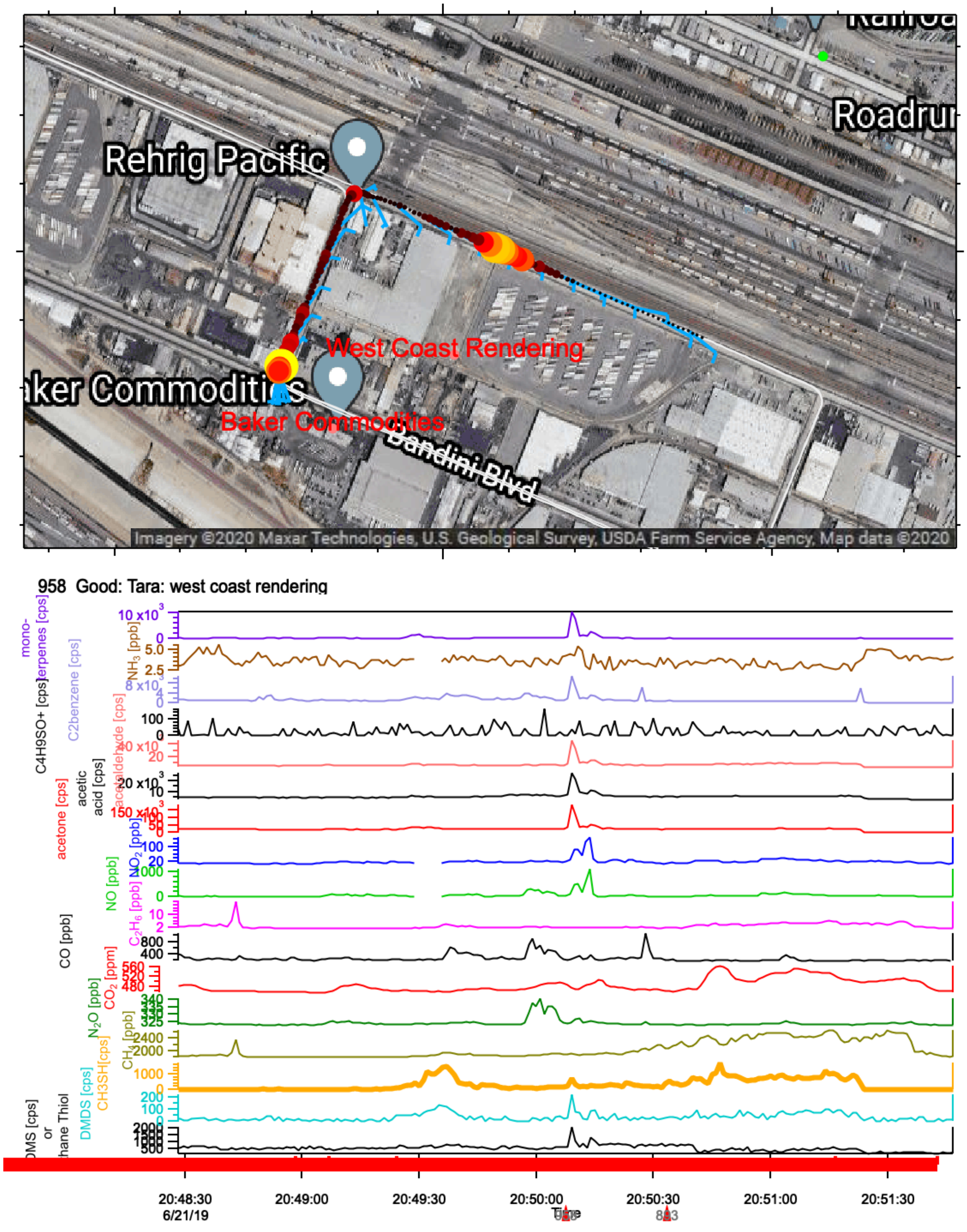

Figure 9. Time series of measurements near West Coast Rendering and Baker Commodities off Bandini Blvd. Methane thiol concentration is shown on the map (yellow-orange-red).

Facilities in this area were noted to be dispersing some sort of material in aerosol form from containers. We expect this is an industrial air freshener of some sort. Indeed, we observe monoterpenes plume with other compounds (Figure 10). It peaks in the NE corner of the transect, near Rehrig Pacific, a plastics manufacturer, but is also present on the northern edge, coincident with but not correlated with methane thiol signal. Acetaldehyde is also present at these locations (Figure 11).

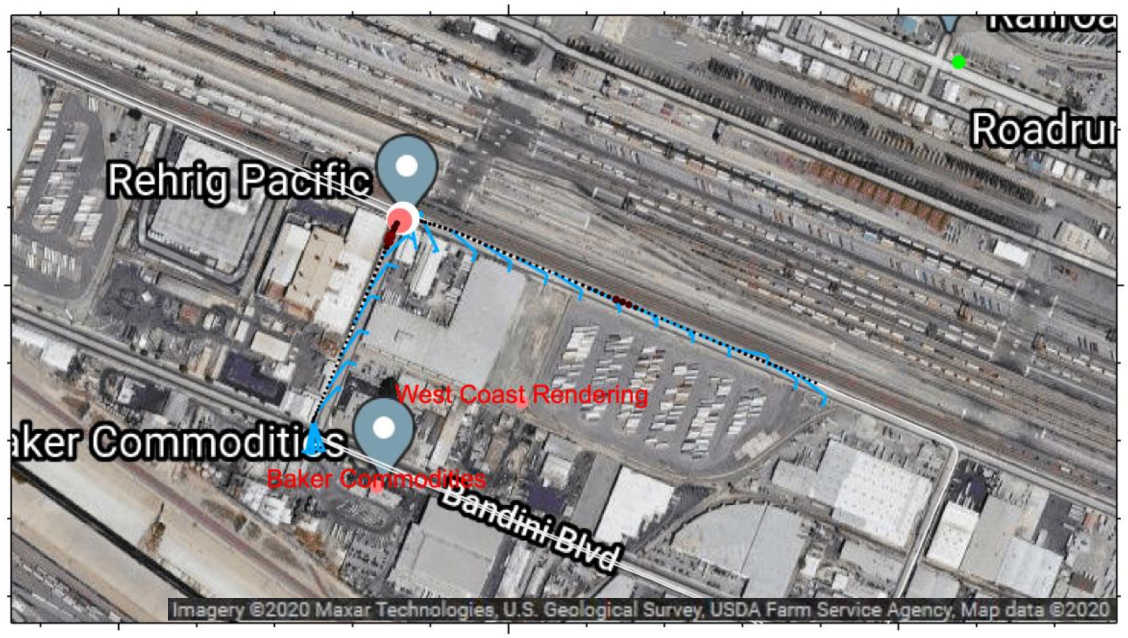

Figure 10. Two areas showing enhanced monoterpenes are shown in the map above. The strongest signal is at the corner, but enhancements are also shown along the northern road, south of the train tracks.

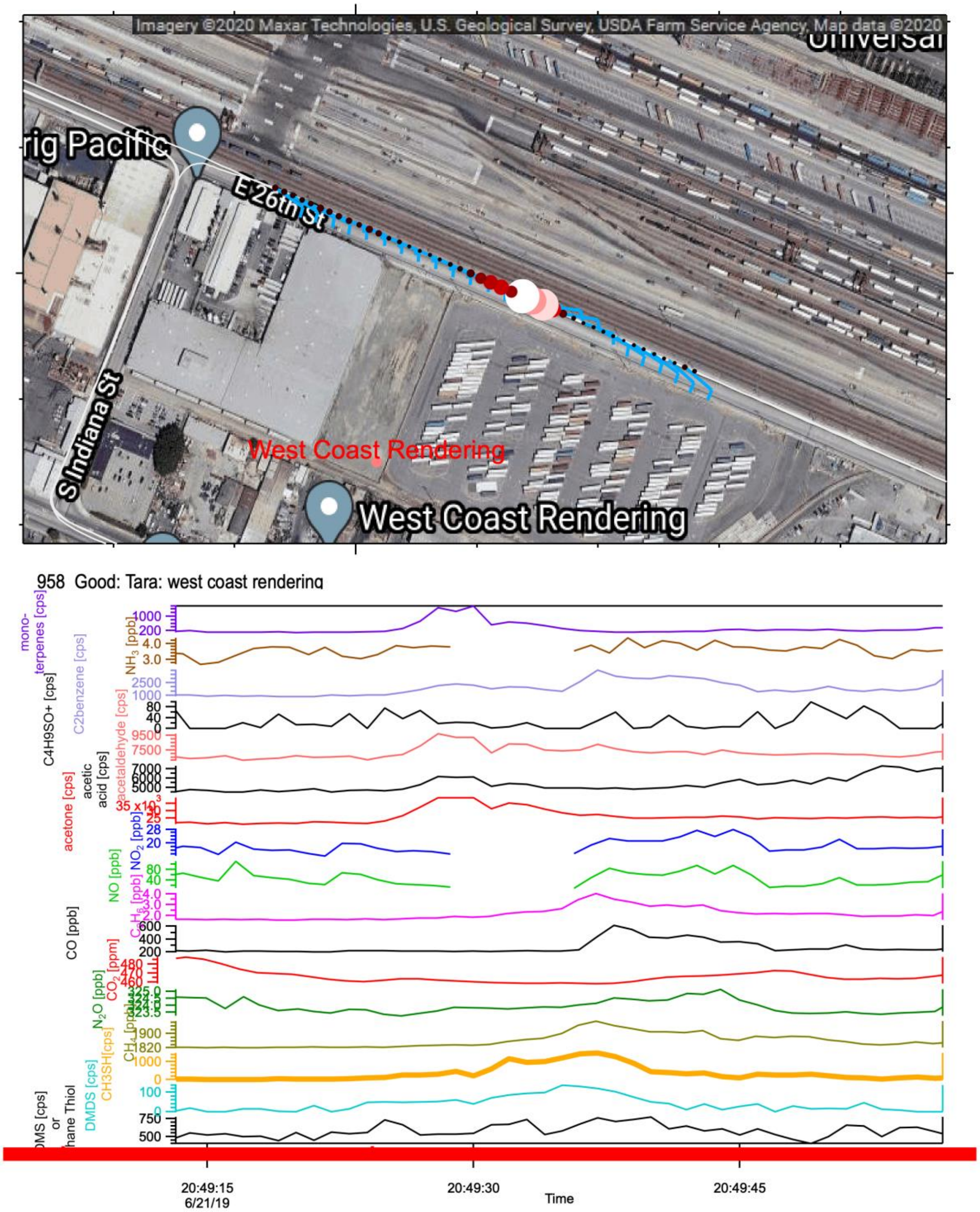

Figure 11. Highlight showing the chemical composition of the monoterpenes signal on E 26th St (mapped in red). Methane thiol is also present, but not well-correlated.

Bandini Blvd: Canister Samples

Two cannister samples were collected at two locations near Bandini Blvd. and analyzed by SCAQMD. These canisters were collected with the AML parked in the odor plume. Analysis results are shown below.

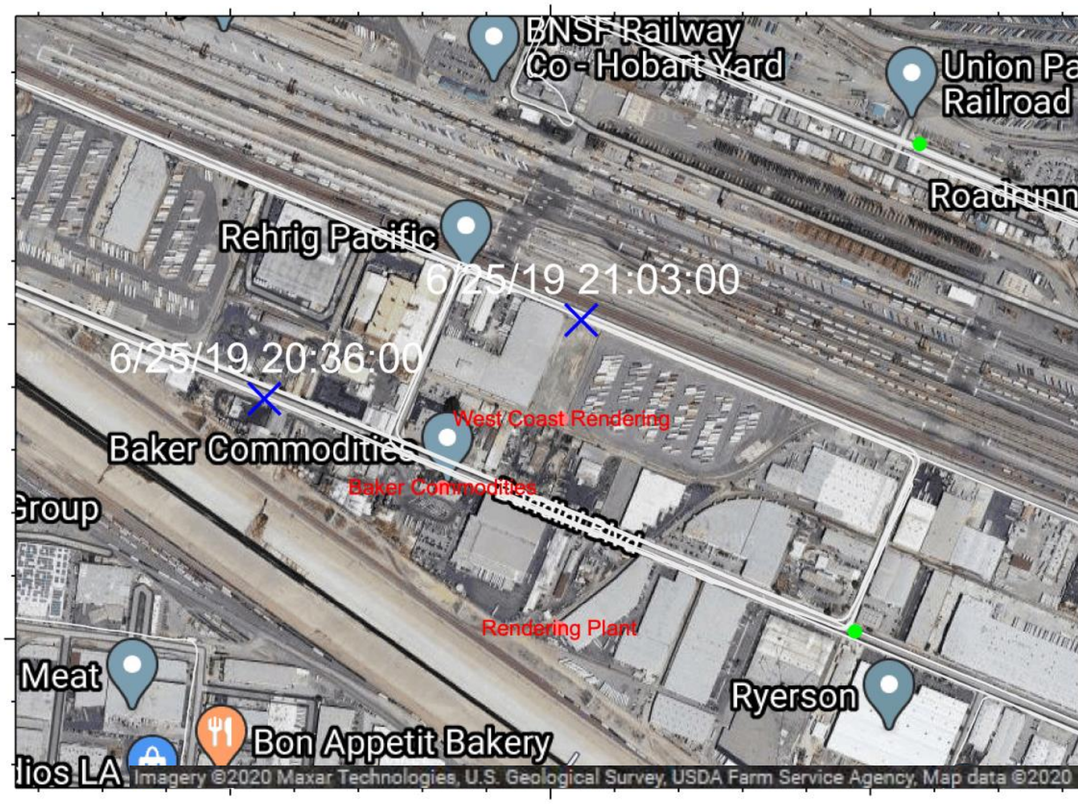

Figure 12. Location (blue X's) and times (white text) of the two canister samples collected.

Table 4. Canister Samples Collected by Aerodyne Research, Inc. and analyzed by SCAQMD.

Location Note	Latitude	Longitude	Canister Label	Canister Analysis ID	Sample Collection Time
Near Baker Commodities	34.00524	-118.19603	ID SM-S1022	1917737-01	6/25/19 20:36:00
Near West Coast Rendering	34.00642	-118.19069	ID 53455	1917738-01	6/25/19 21:03:00

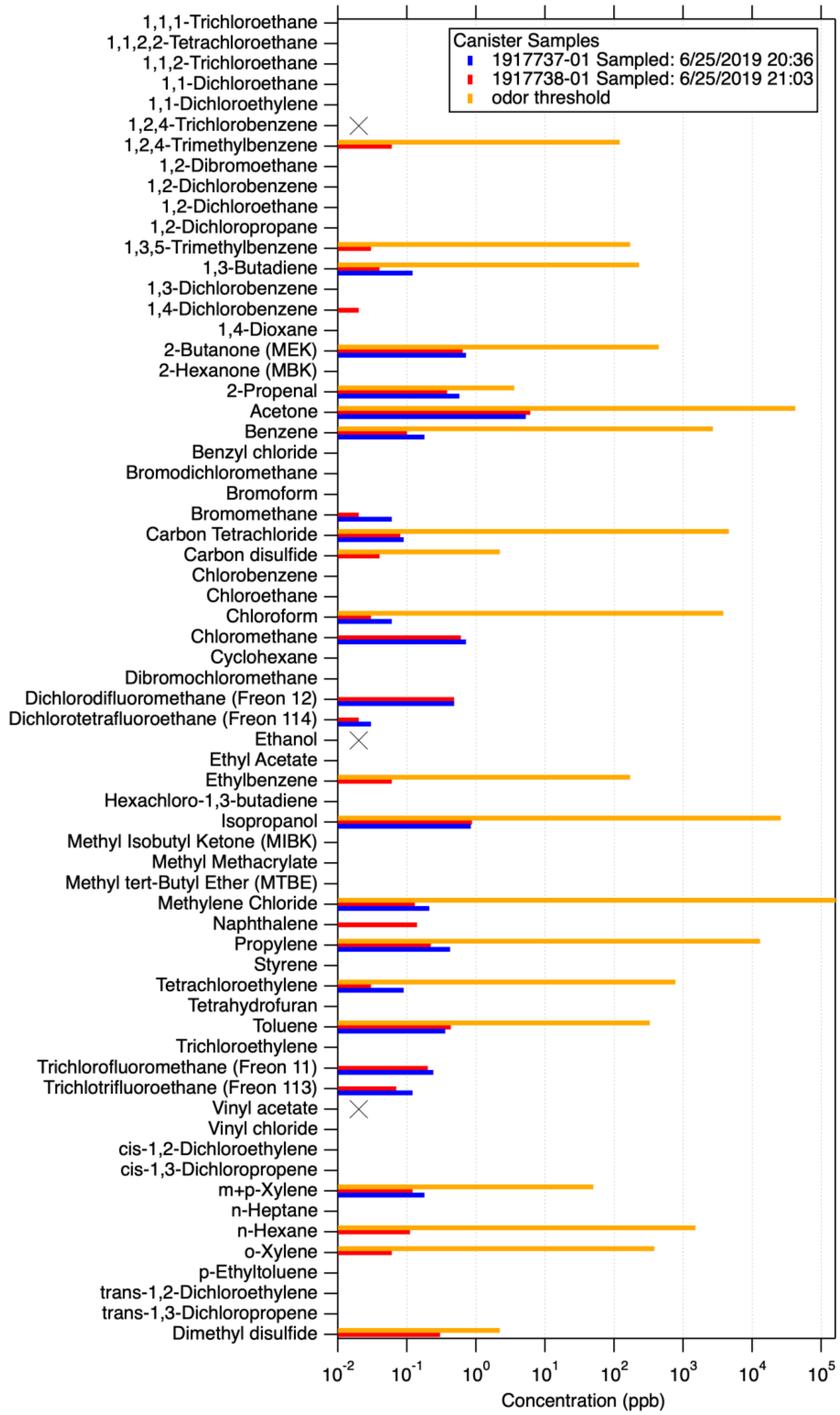

Figure 13. Canister sample results analyzed by SCAQMD. The first sample (blue, 6/25/2019 20:36) was collected on Bandini Blvd near Baker Commodities. The second sample (red, 6/25/2019 21:03) was collected on E 26th St, near West Coast Rendering. Compounds listed as "AS" in the analysis are marked with an X. Compounds listed as "ND" in the analysis are left blank. Dimethyl disulfide is listed as a tentatively identified compound. Odor threshold data from Nagata.[4]

Ketones and aldehydes dominate when it comes to concentrations (acetone, 2-butanone, 2-propenal) and isopropanol also important. No sulfur compounds are included in the standard analysis; dimethyl disulfide is included as a tentatively identified compound in the canister taken (red).

The major difference in these canisters is the presence of dimethyl disulfide (DMDS) in canister 1917738-01 (red), as well as additional aromatic compounds (which may be associated with exhaust). Neither methane nor ethane thiol are reported in this analysis. Despite the measurement team reporting strong odors, none of the compounds analyzed in these canisters exceed odor detection thresholds.[4] Dimethyl disulfide and 2-propenal (aka acrolein) come closest to their odor thresholds. The Vocus instrument, however, measured methane thiol significantly above its odor detection threshold of 0.07 ppb at both canister sampling locations: 0.32 ± 0.06 and 0.34 ± 0.28 ppb respectively (± 1-sigma standard deviation within the heart of the plume). Notably, the Vocus also sees detectable DMS during the second canister, but not the first.

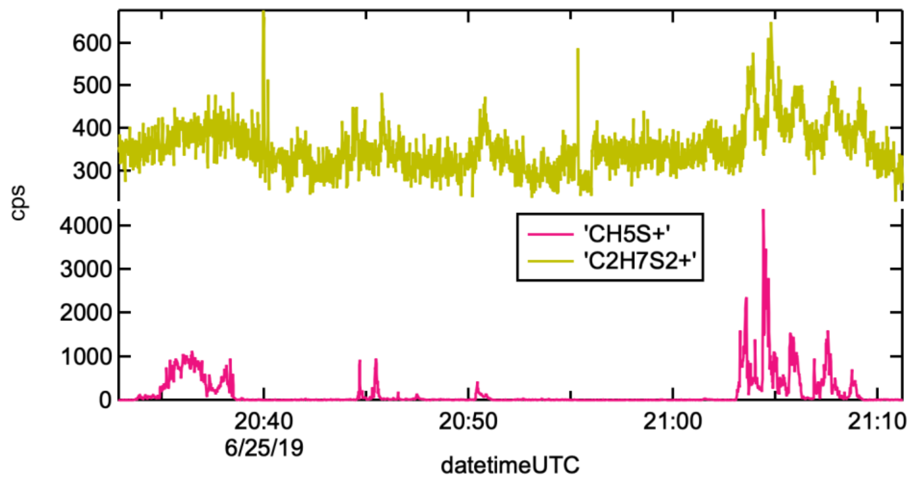

Figure 14. Select Vocus compounds during the canister sampling times. Methane thiol (pink) and dimethyl disulfide (DMS, yellow) are shown.

In summary, the standard GC analysis is not adequate here. More advanced gas-chromatographic techniques are recommended to characterize odor problems, and should include the capability to detect sulfur and nitrogen-containing species.

Darling Delaware

A map of the area around Darling Delaware, an animal rendering facility, is shown below.

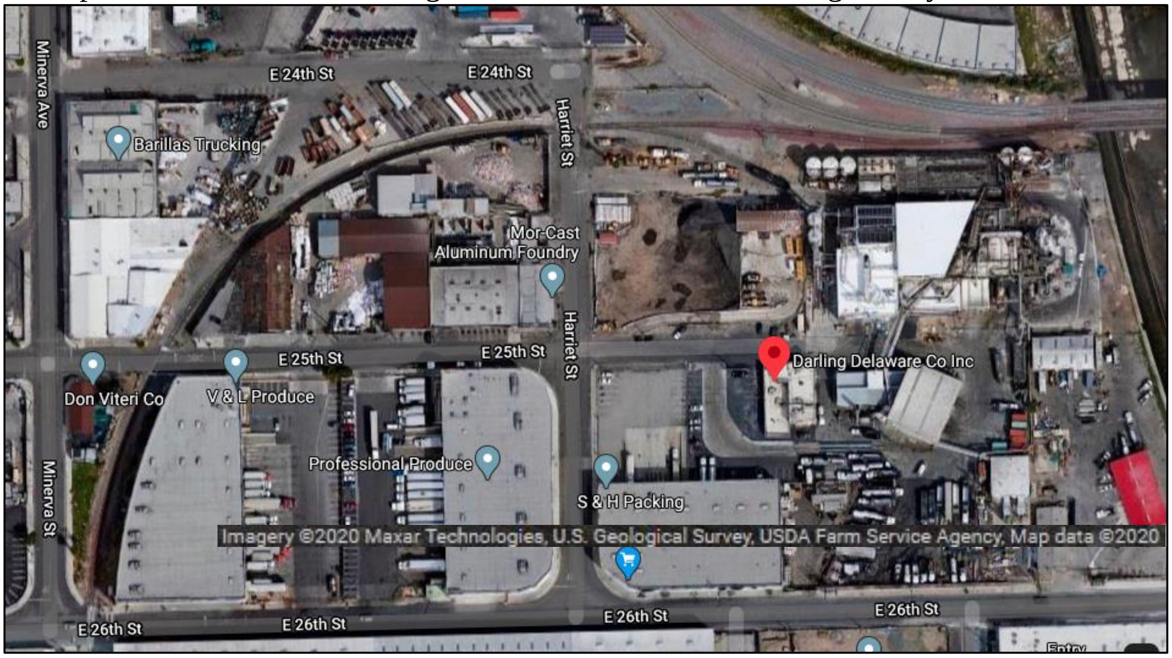

Figure 15. Map of the area around Darling Delaware.

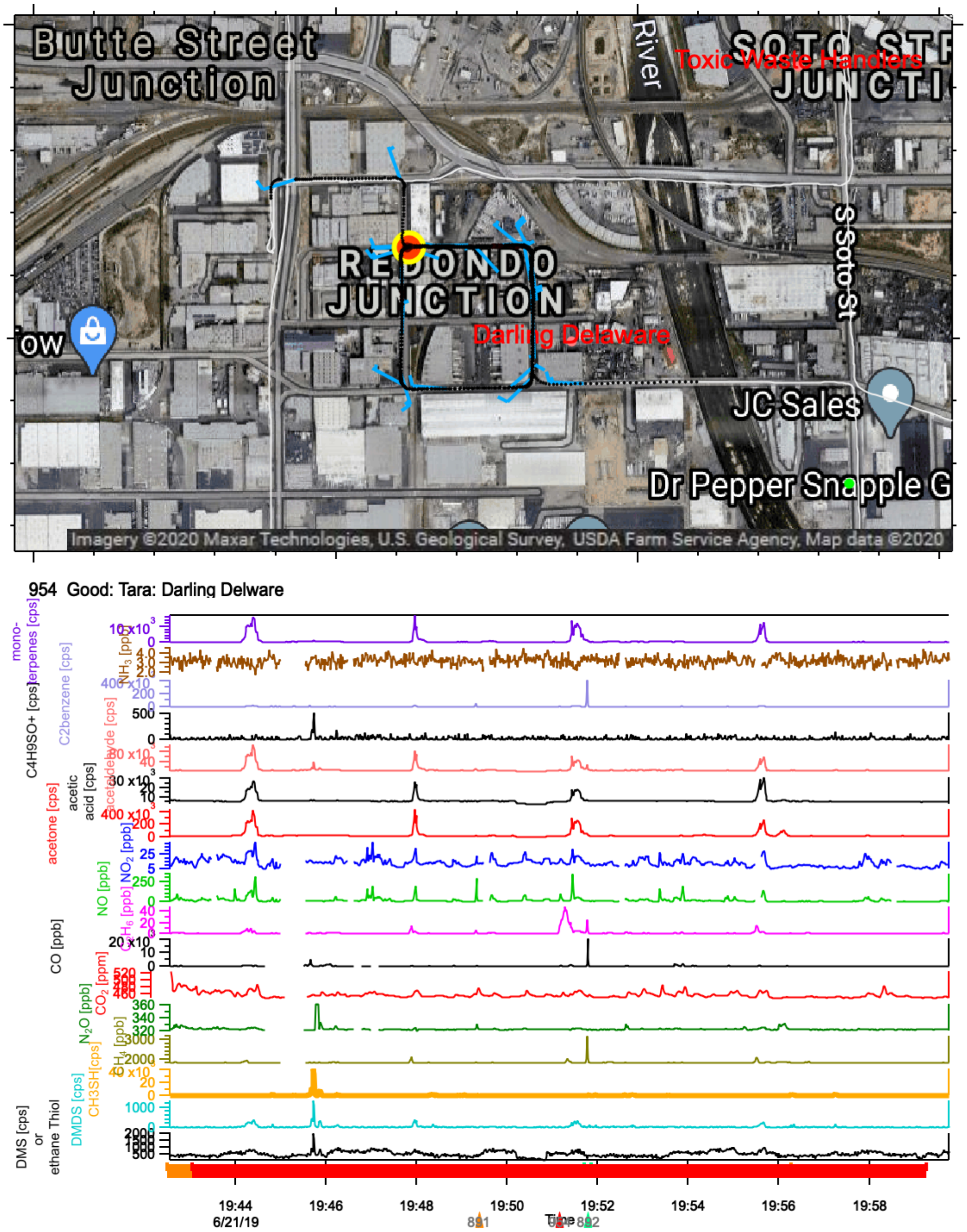

Figure 16. June 2019 transect near darling Delaware. Methane thiol (yellow-orange) is shown on the map.

The above graph shows a spike of methane thiol on the corner of 24th and Minerva Ave (NW corner of the loop). Methane thiol is also present during other portions of the plume.

Figure 17. Transect near the Darling Delaware facility. Acetone is shown on the map.

The graph above shows the acetone trace plotted on the map. Acetone is localized on Harriet St near 24^{th} (NE corner of loop).

Farmer John

Wind during this transect makes it difficult to assign emissions to the Farmer John facility.

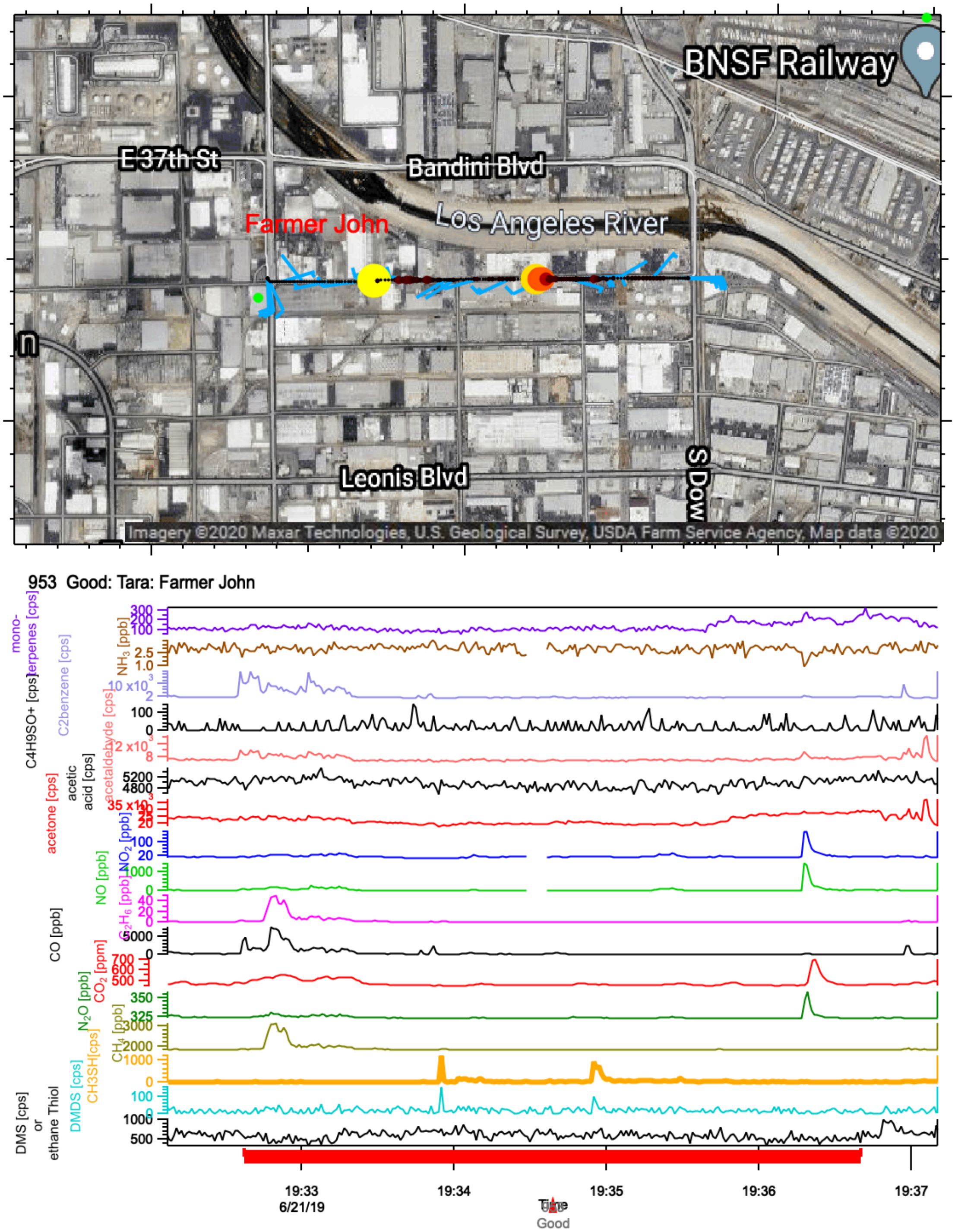

Figure 18. Map of methane thiol (yellow-orange) near Farmer John facility.

Complexity of Odor Plumes

The odor plumes encountered during these measurements were extremely complex. The Vocus relies on mass spectrometry for detection, and hundreds of individual ions were noted during odor plumes. Numerous ion signals were noted had not previously been identified. This is not surprising, since the "peak lists" used by the PTR-MS community to decode the mass spectrum are often based on ambient measurements, or other campaigns focused on more common emission vectors like vehicle exhaust or biomass burning. To our knowledge, this is the first PTR-MS-based dataset on rendering facilities.

At higher masses, the source chemical compound can take on multiple isomeric forms. This adds in an extra challenge when thinking about odor impacts, since these isomers can have vastly different odor detection thresholds, and may smell very different.

The figure below illustrates how isomers can have extremely large variations in odor thresholds. For instance, acetone and propanal (proprionaldehyde) at mass 59 have nearly 5 orders of magnitude difference in their odor threshold. Smaller but significant differences are found in the thiol versus sulfides. Of particular note, both dimethylsulfide and ethyl mercaptan (ethane thiol) have the same mass, but the mercaptan can be detected at significantly lower odor thresholds. Thus, interpretation of the signals depend heavily on what isomeric form is thought to be present.

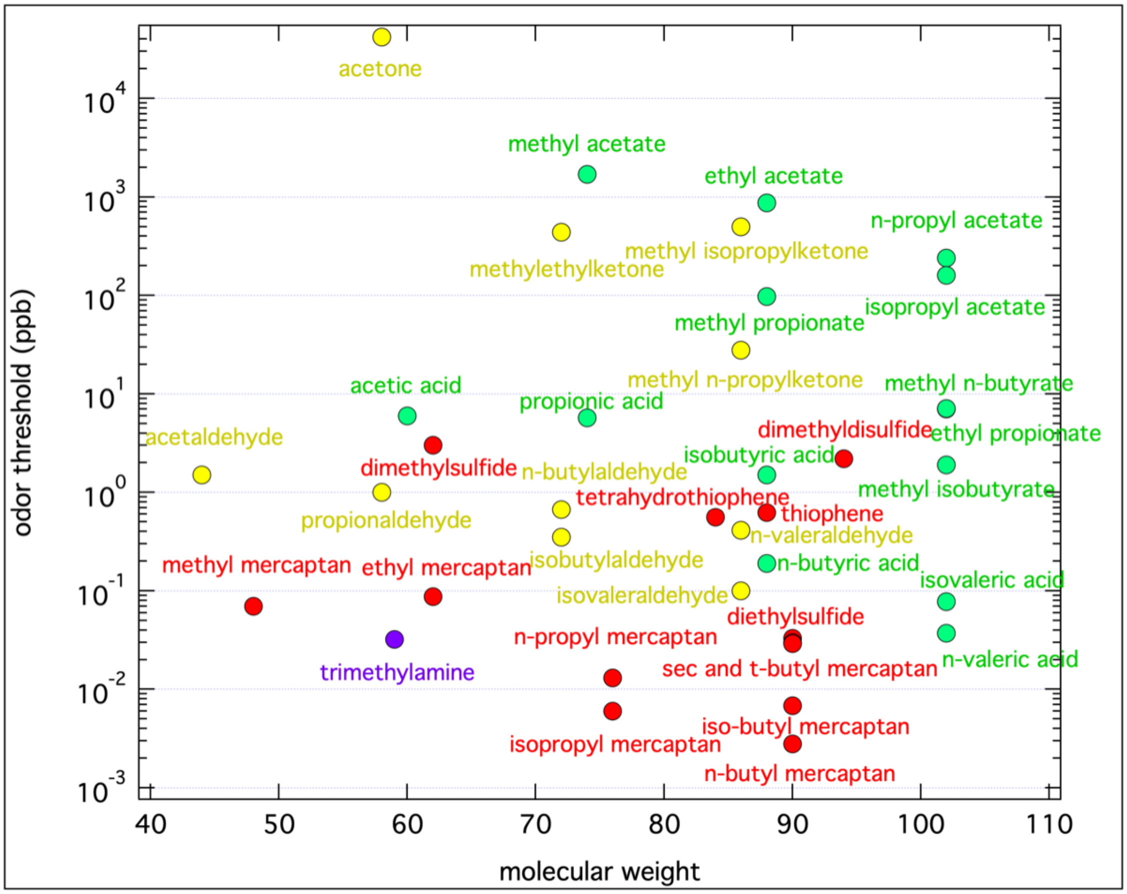

Figure 19. Odor threshold (ppb) versus molecular weight. Mercaptans (thiols) are shown in red; aldehydes and ketones in yellow; amines in purple; all other compounds in green. Note the logarithmic scale for odor threshold.

Figure 19 also illustrates why methyl mercaptan (methane thiol, CH_3SH detected via CH_5S^+) is such a good tracer compound for odor complaints at rendering facilities: it has both a low odor detection threshold and, with its low mass, is unique in the Vocus mass spectrum.

The complexity of the odor plumes are further illustrated in Appendix A, which compares the total mass spectrum taken in the odor plume with a representative spectrum taken of the nearby background.

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